Alkaline Treatment of ARD – Carbonate and Hydroxide Alkalinities in Sequence

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Abstract
Alkalinity generation, alkalinity wash out and neutralizing effect are factors determining the longevity of alkaline filters for ARD-treatment. The focus of this study was to investigate effects of different sequence and mixture of alkalinities. Two different by-products were chosen: one carbonate (WWG) and one hydroxide (LD). Beakers with WWG and LD (1.5 kg in each) were placed in sequence and leached with a diluted sulphuric acid solution (20 mM). Three litres per day were passed through each system, in increments of 0.5 L, during 40 days. Three systems were tested: (1) WWG–LD, (2) LD–WWG and (3) WWG+LD–WWG+LD. Key measurements included pH, alkalinity and selected ions. pH in system 1 was 6 from the WWG and increased to 10 after the LD. pH in system 2 was initially 12 from the LD and 6 from the WWG. The mixtures of WWG and LD were expected to be similar to LD–WWG, i.e. hydroxide buffering at pH 12 followed by carbonate buffering at pH 6. But the mixture of alkalinities was not comparable to any of the sequences of alkalinities. The LD-material was found not to be suitable for this type of ARD-treatment due to vanadium leaching.

Key Words: LD-slag, water works granules, pH, vanadium

Introduction
Abiotic remediation of ARD with barriers and filters (passive systems) are often used in order to minimize the impact on receiving streams, rivers and the wider environment (Johnson and Hallberg 2005). In many cases, pristine raw materials like limestone are used, for instance ALDs and OLDs (Cravotta 2003; Younger *et al.* 2003). At the same time, alkaline secondary materials – by-products – are produced in large quantities at various industries. By-products are cheap alternatives to pristine raw materials like limestone and quicklime and re-utilization of industrial process residues conserves natural resources. A risk associated with using by-products is however that the alkaline materials themselves contribute to release of metals.

The source of alkalinity varies between different materials, and also varies with time due to carbonation. Sartz *et al.* (2010) investigated several alkaline by-products, including fresh and carbonated fly ashes, lime kiln dust, steel slag, lime mud and green liquor dreg and it was found that the alkaline source was the factor having the largest impact on the efficiency of field-scale filters for ARD-treatment. A common problem when treating aluminium- and iron-rich ARD with barriers containing carbonate materials is passivation of neutralising surfaces by hydrolysis products (due to slow carbonate dissolution rates). By keeping reducing conditions while increasing the pH, these problems can be overcome (Cravotta 2003). However, problems with keeping reducing conditions are common. There is also a risk for downstream acidification since latent acidity forms through hydrolysis of aluminum and iron. Neutralisers that contain hydroxide alkalinity dissolve more rapidly and are not likely to be affected by surface passivation of iron- and aluminium precipitates to the same extent as carbonate neutralisers. Drawbacks with hydroxide neutralisers are however initially very high pH, which can increase the mobility of for example lead, as well as rapid alkalinity decrease once the easily dissolved alkali salts are washed out. Low alkalinity can also cause problems with latent acidity in the recipient.

Hydroxide neutralization

The reaction between quicklime and water, the neutralization reaction between the hydrated lime and acid as well as the dissolution of hydrated lime are shown in equations 1, 2 and 3 respectively (Bulusu *et al.* 2007). As hydrogen ions are neutralized by hydroxyl ions, pH increases and dissolved metals are precipitated (Polat *et al.* 2002).

$$CaO(s) + H_2O \rightarrow Ca(OH)_2(s) \quad (1)$$

$$Ca(OH)_2(s) + H_2SO_4 \rightarrow Ca^{2+} + SO_4^{2-} + 2\ H_2O \quad (2)$$

$$Ca(OH)_2(s) \rightarrow Ca^{2+} + 2\ OH^- \quad (3)$$

Upon contact with a low pH ARD that contains significant sulphate concentrations, reaction 3 shifts further to the right, resulting in increased dissolved calcium concentrations. Calcium reacts with sulphate and further hydrate to form gypsum (equation 4) (Shang *et al.* 2006).

$$Ca^{2+} + SO_4^{2-} + 2\ H_2O \rightarrow CaSO_4 \cdot 2H_2O(s) \quad (4)$$

Carbonate neutralization

Reactions between acid and carbonates either neutralize one proton and alkalinity is released in the form of the bicarbonate ion (pH > 6.3) (equation 5), or the carbonate neutralize two protons and carbonic acid is produced (pH < 5.8) (equation 6) (Bellaloui *et al* 1999; Cravotta III and Trahan 1999).

$$CaCO_3(s) + H^+ \rightarrow HCO_3^- + Ca^{2+} \quad (5)$$

$$CaCO_3(s) + 2\ H^+ \rightarrow H_2CO_3^* + Ca^{2+} \quad (6)$$

$$\text{where } [H_2CO_3^*] = [CO_2(aq)] + [H_2CO_3^0]$$

Carbonation

Carbonation of highly alkaline materials, such as steel slag and lime and cement kiln dust occurs as a result of atmospheric CO_2 dissolves into the alkaline solutions and forming new carbonate containing secondary minerals (equations 7 and 8 for formation of calcite from portlandite and ettringite) (Huijgen and Comans 2006; Pérez-López *et al*. 2007).

$$Ca(OH)_2(s) + CO_2 \rightarrow CaCO_3(s) + H_2O \quad (7)$$

$$Ca_6Al_2(OH)_{12}(SO_4)_3{:}26H_2O(s) + 6\ CO_2 \rightarrow CaCO_3(s) + 2\ Al^{3+} + 3\ SO_4^{2-} + 32\ H_2O \quad (8)$$

The aim with this paper was to investigate if it was possible to combine materials with different alkalinities in order to achieve the benefits from both of them. This was done by studying typical representatives of a carbonate material and a hydroxide material placed in different sequences and leached with an artificial ARD. The two materials were chosen because of two reasons: (1) They were typical representatives of a carbonate and a hydroxide material, respectively and (2) they were by-products from other industries, which makes it interesting to investigate possible useful applications instead of depositing the material in landfills.

Materials and Methods

Experimental setup

Three experimental systems were set up in order to study pH and alkalinity in long-term acid leaching of two selected alkaline materials, water works granules (WWG) and LD-slag (LD), typical representatives of a carbonate material and a hydroxide material, respectively. The results of these experiments will become the basis for up-scaling to field-scale and for optimization and selection of alkaline material. The experiment was performed with the WWG and LD in sequence, according to Figure 1. Total mass of alkaline materials in each test container (2 L) was 1.5 kg (dw).

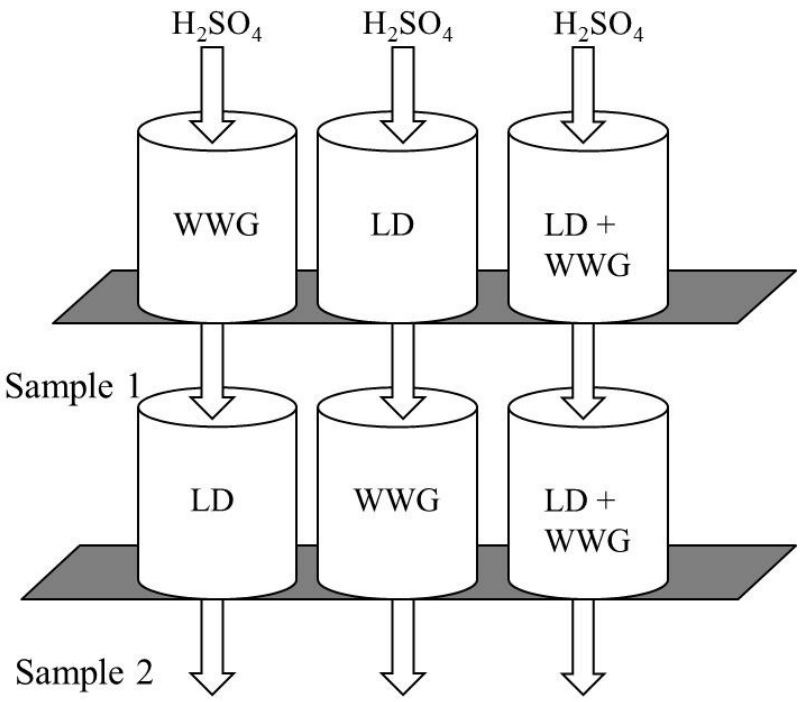

Figure 1. Experimental setup.

LD-slag

LD-slag (LD) is a by-product from the steel industry, the "Linz-Donawitz" process (SSAB Merox AB, Oxelösund). Additives in the process, quicklime, dolomite and oxidizing substances from the rock, eg silica, iron and phosphorous, are components in the LD-slag. It contains some unreacted lime (CaO) resulting in a pH of the final product around 12.3. It also contains several heavy metals (Table 1).

Water works granules

Water works granules (WWG) are produced during softening of drinking water in municipal water works and consist mainly of calcite and magnesite. $Ca(OH)_2$ is added to hard water in a column where silica nuclei are suspended with the aid of compressed air. Due to increased pH precipitation of mainly calcite occurs on the silica nuclei. At a certain weight the granules sink to the bottom of the column and are removed from the system. Leaching data (L/S 10) and total elemental concentrations and buffering capacity together with other general parameters for the materials are shown in Tables 1 and 2, respectively.

Leaching and sampling

The acid leachant was a diluted (20 mM) sulphuric acid. The experiment proceeded for 40 days, with addition of 3 L of 20 mM H_2SO_4 to each system (divided in six portions of 0.5 L each) every day. The leachant was added by gently pouring and the portions were evenly distributed through the day. The leachant was added to the first container (Figure 1) and was allowed to equilibrate for 15 minutes before sampling of 50 mL was performed (sample 1). The remaining leachant was then added to the second container and again allowed to equilibrate for 15 minutes before sampling was made (sample 2). At the end of the experiment, approximately 120 L had passed each test container, representing an L/S ratio of around 80. Only the first samples from each leach day were analysed, while the remaining five samples from each test container were stored (if additional analysis would be necessary).

Table 1. Leaching of elements from alkaline materials at L/S 10 with deionized water (left columns) and total elemental concentrations (right columns). Leaching was performed during 24 hours on an end-over-end shaker. Phase separation was made by centrifugation at 20 000 g for 30 minutes. N.A.: Not analyzed, BDL: Below detection limit.

	Unit	**LD**	**WWG**		**Unit**	**LD**	**WWG**
pH		12.3	6.9				
Alkalinity	(meq/L)	36.6	0.2	Si	g/kg	47.6	52.2
El. cond.	(µS/cm)	9 610	26	P	g/kg	2.46	< 0.1
SO_4^{2-}	(mg/L)	33	N.A.	S	mg/kg	355	346
Ca	(mg/L)	938	9.4	Ca	g/kg	286	355
Mg	(mg/L)	1.2	0.27	Mg	g/kg	63.8	1.39
Al	(mg/L)	0.23	0.54	Al	g/kg	6.36	1.83
K	(mg/L)	2.95	0.96	K	g/kg	0.14	1.52
Na	(mg/L)	3.8	BDL	Na	g/kg	0.17	0.62
Fe	(µg/L)	2 080	203	Fe	g/kg	166	0.51
Zn	(µg/L)	11	BDL	Zn	mg/kg	5.9	2.6
Mn	(µg/L)	BDL	BDL	Mn	g/kg	23.9	0.08
Cu	(µg/L)	1.7	1.4	Cu	mg/kg	6.7	3.6
Pb	(µg/L)	49	0.1	Pb	mg/kg	1.2	0.3
Cd	(µg/L)	0.2	BDL	Cd	mg/kg	0.0	0.1
V	(µg/L)	16.8	0.6	V	mg/kg	17 100	< 2
Mo	(µg/L)	15	1.7				
Cr	(µg/L)	4.0	1.2				

Table 2. Neutralizing potential (NP) and basic physical and chemical characteristics of the materials.

	LD	**WWG**
DW (%)	90	99.8
Bulk density (kg/l)	1.33	1.83
Surface area (m^2/kg)[a]	5	2.8
TOC (%)	<0.21	<1.41
LOI (%)	4.2	38.5
CaO (%)	6.6	<2.4
$CaCO_3$ (%)	5.4	85
NP pH 4 (mole H^+/kg)[b]	6.2	11.0

[a] estimated from grain size distribution
[b] titration to pH 4 for 10 days

Analytical

Electrical conductivity, pH and redox potential were determined immediately after sampling using relevant electrodes. Alkalinity (end-point pH 5.4) was determined through titration with HCl. Inorganic anions (chloride, fluoride and sulphate) were analysed with ion chromatography. Elemental analysis was performed using ICP-MS. All analytical equipment was available at Kopparberg except for the ICP-MS (in a clean room at Örebro University).

Results and Discussion

General parameters and major ions

pH and alkalinity
pH and alkalinity are the two most important parameters when it comes to trace element mobilization/ immobilization. pH determines the speciation and mobility of the trace elements while alkalinity determines how easily pH is changed from its present value. pH and alkalinity in the three systems are shown in Figures 2 and 3, respectively.

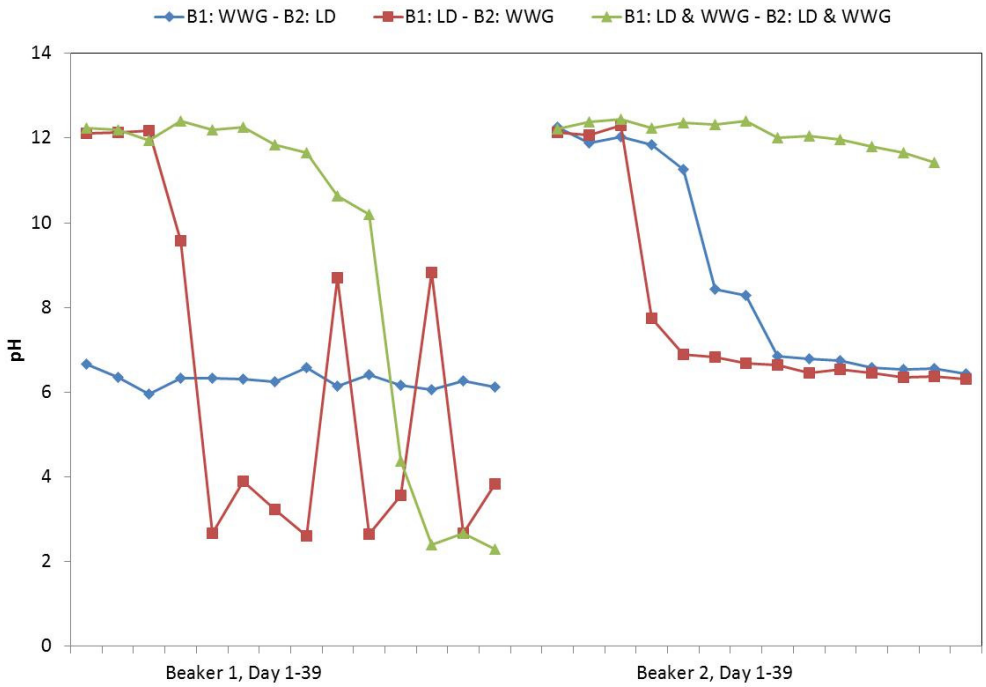

Figure 2. pH in the three different systems from leach day 1 to 39. Blue system is WWG followed by LD, red system is LD followed by WWG and green system is LD and WWG homogeneously mixed in both beakers. B1 is beaker 1 and B2 is beaker 2.

Solution-pH in WWG followed by LD (blue series) was 6 when leaving the WWG beaker and entering the LD beaker (Figure 2). Additional alkalinity from the LD, soluble alkali salts, increased pH to above 10 during the first 20 days of leaching. Thereafter, pH was stabilized to around 6 even after the LD beaker. pH in the LD system, when placed first in the sequence (LD-WWG, red series) was close to 12 during the first 13 days of leaching (Figure 2). Due to the low carbonate content in LD (Table 2), buffering did not take place at pH below 10 and pH dropped rapidly to 2-3. After the first drop in pH in LD (Figure 2, red series), pH was again increasing, at every second or third leach day. The existence of two forms of lime in LD can possibly be the reason for these stepwise pH-shifts: (i) nodules from the addition of lime in excess and (ii) micro-inclusions from the decomposition of the calcium silicate matrix (Waligora *et al.* 2010). This means that a fraction of the LD alkalinity will not be available until some weathering or dissolution has taken place.

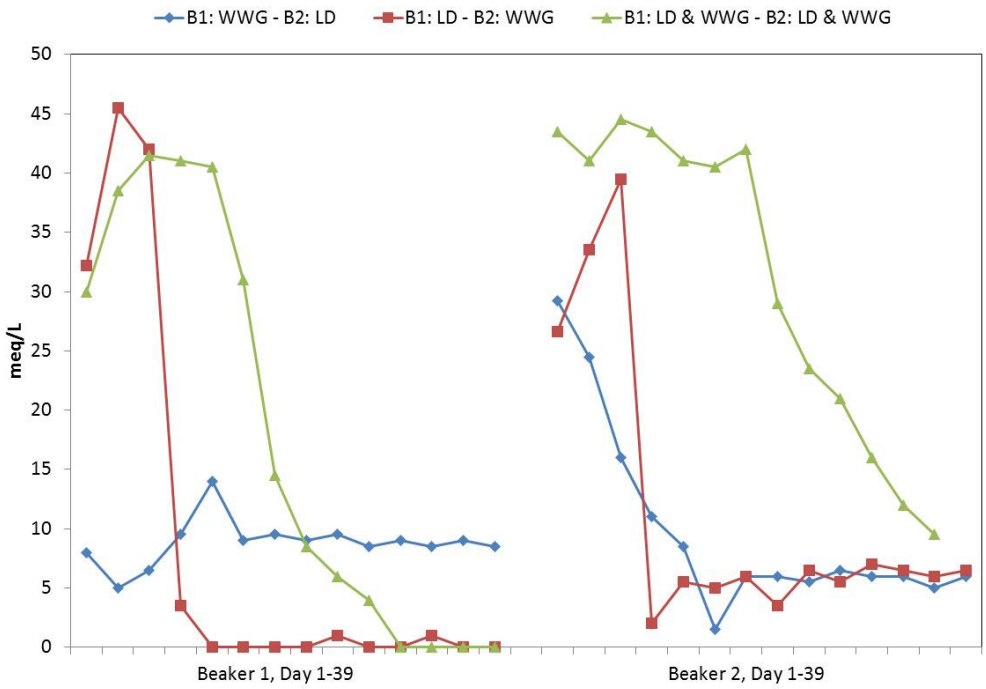

Figure 3. Alkalinity in the three different systems from leach day 1 to 39. Blue system is WWG followed by LD, red system is LD followed by WWG and green system is LD and WWG homogeneously mixed in both beakers. B1 is beaker 1 and B2 is beaker 2.

As long as pH was 12 in the solution leaving the LD and entering the WWG beaker (Figure 2, red series), pH remains high. After the first pH drop in the LD, however (leach day 13 and forward), the WWG buffers the solution to pH 6. The mixtures of WWG and LD (green series) were expected to work similar to the sequence LD – WWG, i.e. first hydroxide buffering at pH 12 followed by carbonate buffering at pH 6. This was however not the case. The mixture WWG+LD was buffering pH at high pH (~12) longer than with only LD, but as the high-pH buffering was depleted, pH dropped down to 2, and no buffering at pH 6 was obtained (Figure 2, green series). The addition of WWG to LD hence supported the buffering at high pH rather than giving the expected buffering steps at pH 12 (LD) and pH 6 (WWG) (Figure 2). This could be due to surface passivation of the WWG in the mixed alkalinities beakers.

Calcium and iron

Calcium concentrations were highest in the LD+WWG-system (Figure 4, left, green series), and were in agreement with alkalinity measurements, ie buffering from calcium minerals ($Ca(OH)_2$, $CaCO_3$ as well as secondary calcium minerals). Iron is present in low concentrations in WWG and very high concentrations in LD (Table 1). Leached concentrations of iron were accordingly very high from the LD-material and very low from WWG (Figure 4, right).

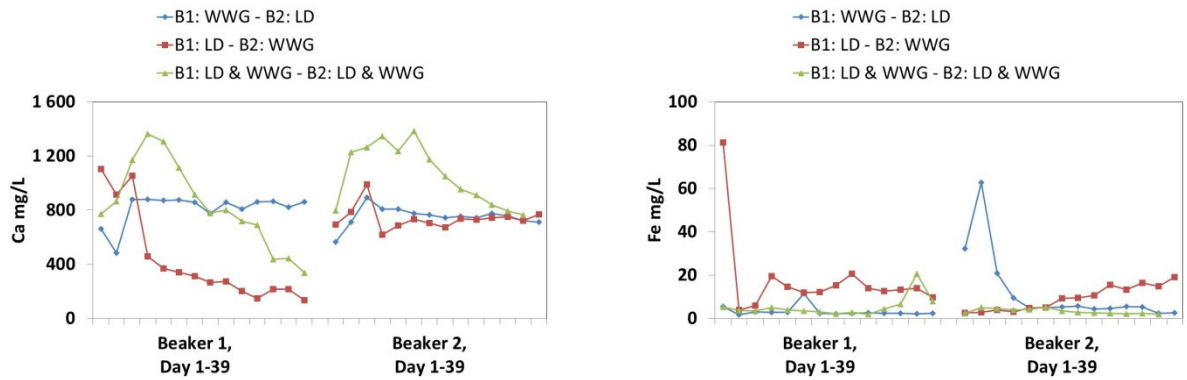

Figure 4. Concentrations of calcium (left) and iron (right) in the three different systems from leach day 1 to 39 (mg/L). Blue system is WWG followed by LD, red system is LD followed by WWG and green system is LD and WWG homogeneously mixed in both beakers. B1 is beaker 1 and B2 is beaker 2.

Alkalinity wash out

In addition to the neutralization reactions consuming buffering capacity, large amount of buffering capacity was also washed from the materials as alkalinity in solution. Figure 5 shows the cumulative wash out of alkalinity (in meq) from the systems.

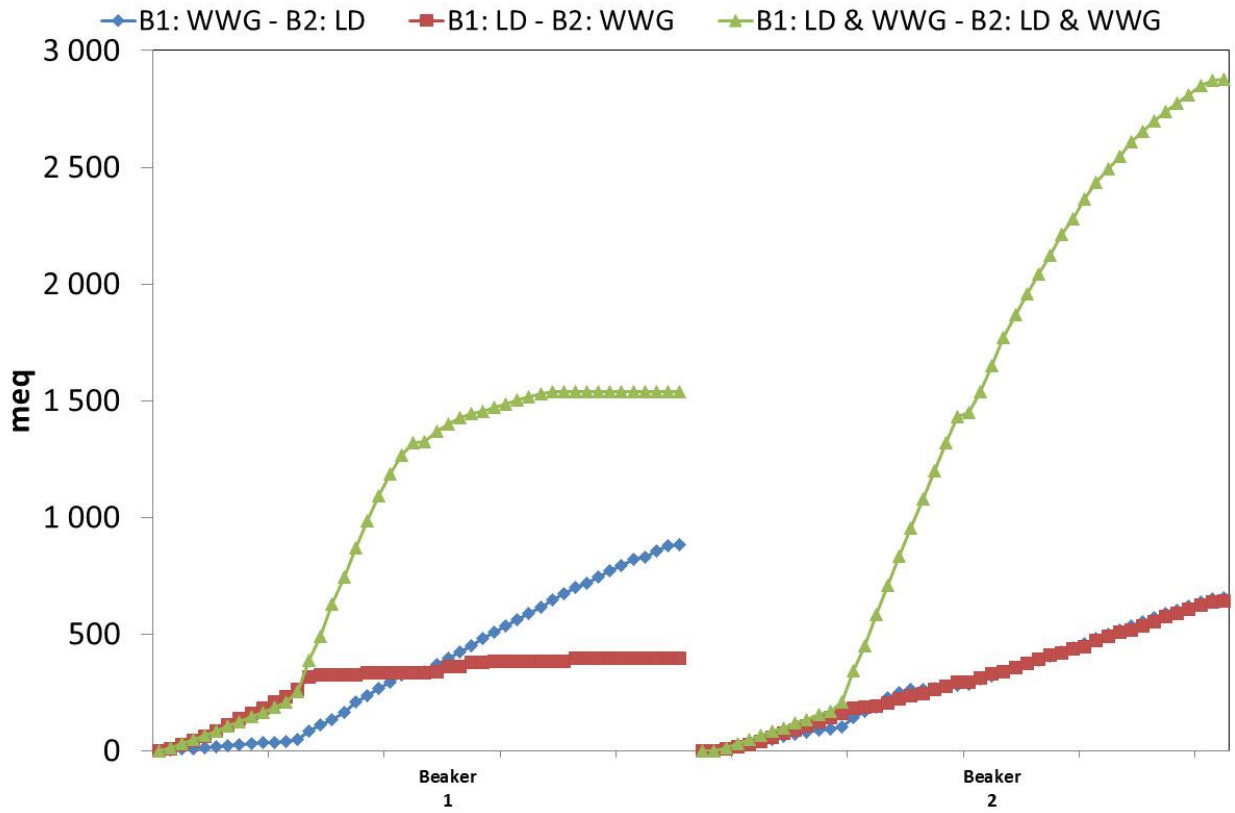

Figure 5. Alkalinity wash out (in meq) in the three different systems from leach day 1 to 39. Blue system is WWG followed by LD, red system is LD followed by WWG and green system is LD and WWG homogeneously mixed in both beakers. B1 is beaker 1 and B2 is beaker 2. Total neutralizing capacity was 9 300 mmol H^+, 16 500 mmol H^+ and 12 900 mmol H^+ in each of the LD, WWG and LD+WWG test containers, respectively (table 2, titration to pH 4). At the end of the experiment approximately 2 400 mmol H^+ had been added to each system.

Figure 5 clearly shows that in the system with mixed alkalinities (green series), large amounts of available alkalinity was washed out, with no use. This behavior would be fatal in a field scale filter, as the calculated total neutralizing capacity would be overestimated and the filter would not be able to neutralize as much acidity as it was designed for.

Trace elements

As the focus of this study was to study the effects of different sequence and mixture of alkalinities, mainly in the manner of alkalinity generation, alkalinity wash out and neutralizing effect – effects that determine the longevity of a filter – were the most important parameters to evaluate. Therefore, the leach solution used (the artificial ARD) was neither added any trace metals, nor iron. In follow up experiments, these constituents should be added; alternatively, a real ARD could be used. Consequently, in the evaluation of trace element behavior in the present experiment, only the ones already present in the alkaline materials will be discussed. Trace element leaching from the alkaline materials is as well an important parameter to evaluate, as the tested alkaline materials are by-products from other industries and a new source of pollution is not wanted.

Trace elements of interest for these materials were: copper, zinc, lead, chromium and vanadium (LD only) (Table 1). During the experiment concentrations of copper, zinc and lead were low, some wash out effect was however seen for these elements during the first days of leaching, with maximum values of 120 µg/L, 800 µg/L and 20 µg/L for copper, zinc and lead, respectively. Initial was out of chromium (~1 000 µg/L) was noted in the LD-containing test containers. The concentrations of chromium however rapidly decreased, and were constantly low from the third leach day and forward. Vanadium leaching from the LD-containing test containers was on the other hand substantial (Figure 6) and the leaching pattern differs between the different systems.

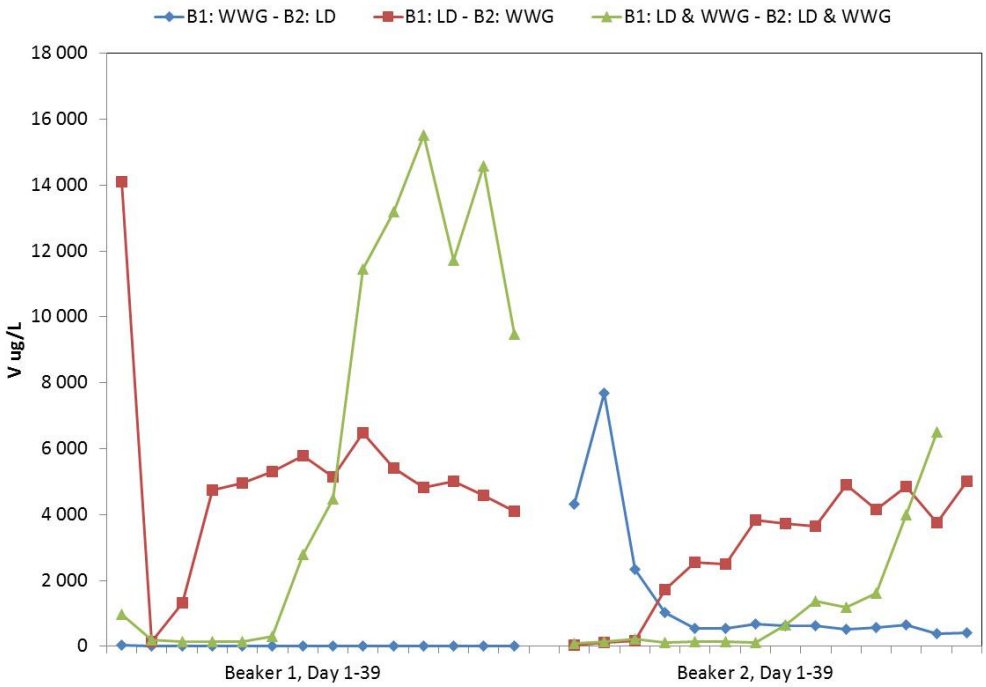

Figure 6. Vanadium concentrations (µg/L) in the three different systems from leach day 1 to 39. Blue system is WWG followed by LD, red system is LD followed by WWG and green system is LD and WWG homogeneously mixed in both beakers. B1 is beaker 1 and B2 is beaker 2.

Vanadium is probably originally present as a calcium vanadate ($Ca_2V_2O_7$) in the slag (Cornelis *et al*. 2008; Aarabi-Karasgani *et al*. 2010). Dominance of V(V) in initial leaching stages of LD (pH > 9) has previously been confirmed by Sjöberg *et al*. (2010) and the leaching of vanadium is suggested due to a kinetically controlled dissolution from a not yet identified solid phase. Immobilization of vanadate normally takes place at pH below 10, by sorption onto hydrous ferric oxides (Peacock and Sherman 2004; Rietra 2001; Wehrli and Stumm 1989) (Figure 7). This is however not seen in the present experiment. It was expected that vanadium concentrations would decrease in the second beaker of the LD – WWG series (red series), as pH dropped down to 6 (Figure 2). But once the vanadium was mobile, it continued also through the second beaker (Figure 6).The lack of iron in the added ARD, and therefore lack of surface sites, could be an explanation.

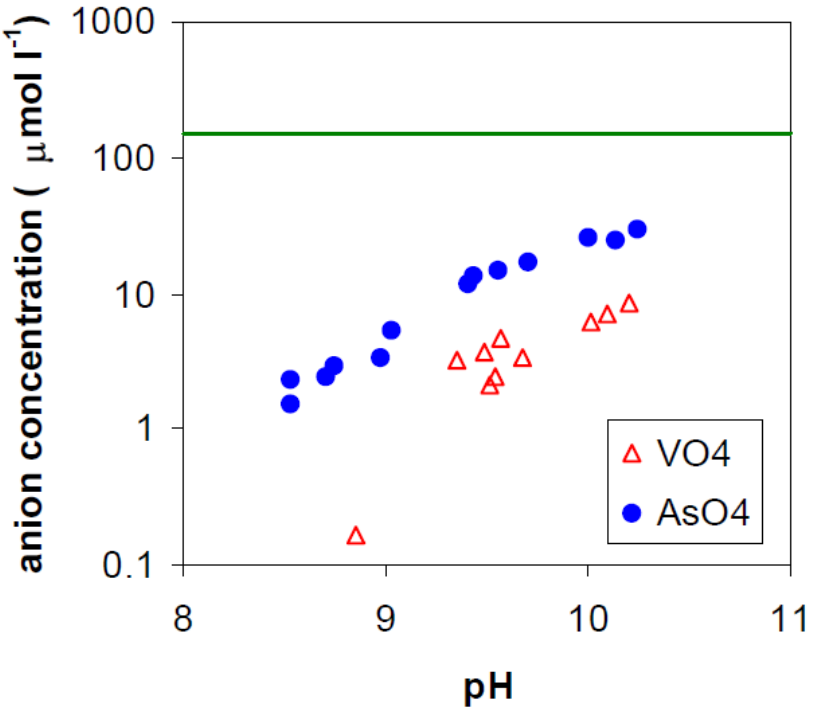

Figure 7. VO_4 and AsO_4 concentrations after equilibration of 150 µmol/L VO_4 or AsO_4 with 1.62 g/L goethite. 0.01 mol/L $NaNO_3$ was used as background electrolyte. The green line indicates the added concentration of VO_4 or AsO_4 (150 µmol/L). The figure is redrawn from Rietra (2001).

Conclusions

The aim with the experiment was to find an optimal sequence of alkalinities that would combine alkalinity from a carbonate material (WWG) and a hydroxide material (LD). However, neither any of the sequences of alkalinities nor the mixture of alkalinities gave any promising results to speak of:

- The WWG – LD series was the most stable system, with pH above 6 and high alkalinity throughout the whole experiment. The LD (beaker 2) did however not contribute to any greater extent and was more or less unnecessary.
- The LD – WWG series gave initially high pH and alkalinity from the first beaker, but the alkalinity was washed out rather fast. pH and alkalinity were then stabilized in the second beaker (WWG). Again, the LD did not contribute to the end result to any greater extent.
- The mixture of alkalinities drastically increased the alkalinity wash out, which in turn affect the longevity of a filter (alkalinity is washed out without neutralizing any acid). The expected

buffering steps at pH 12 and 6 in the LD+WWG series did not occur, maybe due to surface passivation of the WWG.

Vanadium was leached at high concentrations from the LD-slag. This makes the LD-slag unsuitable for this type of application (ARD treatment).

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